Changes in the binding form of copper and zinc in sewage field soil by addition of biochar after eight years of field exposure

Anne Wagner, Anne Müller & Martin Kaupenjohann
Background & Hypothesis

In previous field studies we analyzed the short-term effects of biochar (BC) on heavy metal mobility on former sewage fields Schweiker et al. (2014), Wagner & Kaupenjohann (2015)

Now we are interested in aging of heavy metal binding form under field conditions.

We hypothesise that BC causes shifts from weaker to stronger heavy metal binding forms.
Materials and Methods

Soil

from sewage field with 0% and 5% biochar addition taken 2011, 2013 and 2019

Sequential extraction procedure (Zeien and Brümmer, 1989) slightly changed

| I  | in water-soluble and exchangeable form |
| II | in easily available and mobilizable form |
| III | bound to Mn oxides |
| IV | bound to organic matter |
| V  | bound to amorphous iron oxides |
| VI | bound to crystalline iron oxides |
| VII | bound in residual forms (calculated from total content determined separately by digestion with aqua regia minus metal in other fractions) |
Soil total Cu concentrations

significantly decreased from 2011 to 2019 without BC addition

(mean 13% = 44mg/kg)
Soil total Cu concentrations significantly decreased from 2011 to 2019 without BC addition (mean 13% = 44mg/kg) but not with BC - Why?

10 % tolerance in measurement accuracy, ... anything else?
Soil Cu 2019

With BC:
Only small changes in Cu binding form

higher Cu content in residual fraction with BC-
due to lower total Cu concentrations in 0%

Means and standard deviation

T-test
Soil Cu in mg/kg
2011 vs 2019

Means and standard deviation
Paired t-test

Another mechanism which prevents loss of Cu from stock?
Another idea how biochar might prevent loss of Cu?

Porous BC particle

Metal

Organic coating of pores

Time after BC addition
Successive extraction of aged BC

0.5 g Biochar particles (>1mm) picked from sewage field with 5% biochar addition after 8 years of field exposure

<table>
<thead>
<tr>
<th>Treatment</th>
<th>1. Extraction</th>
<th>2. Extraction</th>
<th>3. Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>mild oxidation</td>
<td>Cu in H2O2</td>
<td>Cu in H2O2</td>
<td>Cu in H2O2-HCl</td>
</tr>
<tr>
<td>Control</td>
<td>Cu in H2O</td>
<td>Cu in H2O</td>
<td>Cu in H2O-HCl</td>
</tr>
<tr>
<td>H2O2</td>
<td>Extraction 12.5ml 0.8 mMol HCl 23h</td>
<td>Extraction 12.5ml 0.8 mMol HCl 23h</td>
<td>Extraction 12.5ml 0.8 mMol HCl 23h</td>
</tr>
<tr>
<td>5ml</td>
<td>45 min.</td>
<td>45 min.</td>
<td>45 min.</td>
</tr>
<tr>
<td>H2O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5ml</td>
<td>45 min.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Cu in biochar particles 2019

Solution from treatment

Solution from HCl extraction

Means and standard deviation

T-test
Cu in biochar particles 2019

Cu remobilized from biochar particles in % of total soil Cu (sum of three extractions)

- H2O and HCl: 1.2%
- H2O2 and HCl: 22%

Preliminary results unfortunately due to corona lockdown total Cu content of BC particles could not be determined yet.
Zn in biochar particles 2019

Solution from treatment

Solution from HCl extraction

Relative to Cu, more Zn mobilized with HCl in H2O treatment

In contrast to Cu, no significant effect of treatment in 3. extraction

Zn is found inside and on the surface of BC particles which dissolves successively with each extraction step

Means and standard deviation

T-test
Zn in biochar particles 2019

Preliminary results unfortunately due to corona lockdown total Zn content of BC particles could not be determined yet

Relative to Cu, more Zn in or on BC particles

Solution from treatment

Solution from HCl extraction

Means and standard deviation

T-test

Zn remobilized from biochar particles in % of total soil Zn (sum of three extractions)

H₂O and HCl
24%

H₂O₂ and HCl
74%

1. extraction  2. extraction  3. extraction
Summary and Conclusions

(1) BC reduces loss of Cu from stock

(2) This is not seen in an increase of Cu in stronger binding forms according to Zeien and Brümmer

(3) We assume that Cu und Zn diffuse in pores of BC and are fixed and trapped inside
Thank you!